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DIRECT ENERGY CONVERSION IN THE USSR

ASTIA No. SOLAR CELL RESEARCH
Comprehensive Report

AID Work Assignment No. 21

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SOLAR CELL RESEARCH

Comprehensive Report

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FOREWORD

This is the first report prepared in response to AID Work Assignment No. 21. The source material used for the report was published during 1961 and 1962, with the exception of certain background material published earlier.

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INTRODUCTION

The development of methods for direct conversion of solar energy into electric power was one of the major tasks assigned to Soviet science workers by the party program published in July 1961 and adopted the following October by the Twenty-Second Congress. Speaking before the Congress, M. V. Keldysh, President of the Academy of Sciences USSR, stressed the "colossal possibilities offered by research in the field of solid state physics" [1], and this view has since been steadily developed in magazine and newspaper articles. Statements appear on "the great progress in research on the use of solar energy" connected with establishment, within a single year, of heliolaboratories in the Armenian, Georgian, Turkmen, and Uzbek Republics [2]; on plans completed by the Uzbek Academy of Sciences for the construction of a solar power plant which would utilize silicon semiconductors with a total battery surface of 10 m² to produce 5 kw [3]; on the successful production at the Institute of the Laboratory of Semiconductors, Lithuanian Institute of Physics and Mathematics, of thin CdTe films with great potential value for the development of solar batteries [4]; and on a 2.2 million kilowatthour solar power plant to be built under the direction of the Soviet solar cell expert V. A. Baum in the Ararat Valley in Armenia [5]. More distant plans are reflected in a popular article in which Academician Semenov envisions the construction on the moon of a giant photocell-operated power plant with a capacity exceeding that of all power plants now existing on earth [6].

The strong emphasis laid in the USSR on large-scale development of systems for direct solar energy conversion raises the question of existing potential for rapid progress in this field. A few remarks on past achievements and the work of Soviet scientific personnel may furnish a background for measuring present capabilities.

Led by A. F. Ioffe, "the father of semiconductors," a small group of Russian sementists, which included V. D. Kuznetsov, who is the author of basic works on solid state physics, and A. B. Shubnikov, dean among crystallogaphers, has worked since prerevolutionary days toward developing what has become modern semiconductor physics. After the revolution the group grew larger and in the thirties the Soviet Union ranked high in semiconductor research. Many of Ioffe's ideas, particularly his hole-electron concept, were universally adopted; Ya. I. Frenkel, author of the exciton theory, became recognized as one of the top experts on the band theory and the electron processes in solids; I. K. Kikoin discovered the photoelectromagnetic effect; V. Ye. Iashkarev, B. M. Vul' and, somewhat later, S. M. Ryvkin gained prominence as investigators of various semiconductor properties; A. A. Lebedev became an international authority on photoelectric processes and Ye. F. F. Gross on solid state spectroscopy.

After World War II and the attendant disruption of the normal evolution of Soviet scientific endeavor, a comeback was staged, again at the initiative of Ioffe, in 1951, when the Academy of Sciences USSR established in Leningrad the Laboratory of Semiconductors affiliated with the Physicotechnical Institute which now bears Ioffe's name. In 1954 the Laboratory became the Institute of Semiconductors with Ioffe as its first director. The first issue of the specialized Journal of Solid State Physics (Fizika tverdogo tela), edited by Ioffe, appeared in 1959.

While some of the older scientists are still very active, Soviet semiconductor physics are at present dominated by an impressive array of new names. The following scientists may be singled out as being at the top of the hierarchy because of the leading positions they hold in various branches of semiconductor physics directly or indirectly concerned with the photovoltaic effect.

- Yu. P. Maslakovets, Ioffe's pupil and collaborator, is still probably the highest authority on photovoltaic cells in the USSR. Since 1959 he appears to be at the head of an important CdTe project.
- V. K. Subashiyev is the top expert on silicon photovoltaic cells. There are indications that with V. S. Vavilov and A. P. Landsman, Subashiyev designed the silicon solar energy converters for the first sputniks. Vavilov, more recently, has conducted extensive studies of the effects of electron and neutron bombardment of silicon photoelements, while Landsman is working with V. A. Baum in Uzbekistan on solar power station projects.
- S. M. Ryvkin, an authority on extrinsic photoconductivity, is a prominent theoretician in the field of the photovoltaic effect. Academician V. Ye. Lashkarev is the expert on CdS.

To this group might be added the names of V. M. Malovetskaya, who may have participated in preparing Si photocells for the sputniks, G. N. Galkin and Ye. L. Nolle, who are authorities on Si, and D. N. Nasledov, who during the last five years has published a large number of papers on GaAs and Ind InSb.

I. BASIC RESEARCH

At the time of the launchings of the first sputniks, the splution of the following three problems was considered by leading Soviet solar cell researchers to be of prime importance: 1) the "anomalous" decrease of electron lifetimes after thermal diffusion of phosphorus into silicon which, as had been established, could not be caused by the presence of phosphorus atoms; 2) the comparatively poor spectral response of the available silicon solar batteries in the higher frequency region, a deficiency unexplainable by the process of photoionization; and 3) the difficulties of reducing the reflection coefficient without increasing the velocity of surface recombination [7]. In trying to solve any one of the above problems, the scientists ere necessarily hampered by the shortcomings of existing semiconductor theory, and their statement therefore indicates that the principal trend of Soviet research on the photovoltaic effect is to gain a better understanding of the basic principles underlying the processes of the absorption and utilization of photon energy for the creation of electron hole pairs. This the Russians have endeavored to achieve by devoting a remarkably large part of their efforts during recent years to basic investigations not aimed at obtaining immediate practical results.

The theoretical studies of the photovoltaic effect are today centered at the Physicotechnical Institute imeni A. F. Ioffe and the Institute of Semiconductors, both of the Academy of Sciences USSR and both located in Leningrad, and the Physics Institute imeni P.N. Lebedev in Moscow. These three institutes account for more than half of all basic work done in this field by the 25 Soviet research centers directly or indirectly concerned with the development of solar batteries. However, theoretical studies are carried out in practically all the other scientific institutes enumerated in the present survey.

Energy band structures, as well as methods for their study, have been the subject of continuing general work. F. M. Gashimzade of the Physics Institute of the Azerbaydzhan Academy of Sciences and V. Ye. Khartsiyev of the Physicotechnical Institute in Leningrad devised a modified orthogonolized-plane-wave method for band structure calculation [8]. They substituted the Slater function for the wave function in computing the energy bands of silicon, germanium, and gallium arsenide. The results obtained for Si and Ge agreed satisfactorily with calculations made by other researchers, and application of the new method was suggested for computation of complex semiconductor compounds, the energy structure of which Gashimzade described in a separate paper [9].

Yu. M. Butusov and M. V. Kopytina of Voronezh State University examined the objections raised to the approximation method (substitution of E_{Φ} for E_{Φ} in the Schrödinger wave equation) customarily used for solving the band theory problem of a system of N interacting conductivity electrons and demonstrated that the method is mathematically justified [10].

In an attempt to construct a unified band theory for liquids, amorphous bodies, and disordered alloys, A. I. Gubanov included crystals with structural defects and investigated the energy spectrum in the

second approximation with respect to the parameters which characterize the degree of disorder in the system [11, 12].*

A comprehensive analysis of semiconductor imperfections was conducted by V. L. Bonch-Bruyevich of Moscow State University. In a paper written with Vi B. Glasko, Bonch-Bruyevich reviewed the general properties of the electronic energy spectrum in crystals containing extensive structural defects [13]. Calculations were made of the hole levels connected with purely linear dislocations in n-type germanium and silicon. Only edge dislocations which were macroscopically homogeneous and free of impurity atmospheres were examined. Screw dislocations were the subject of a second study, in which the model of a "charged line" used previously had to be discarded since a screw dislocation does not contain vacant hands and the energy of the interaction of the carrier with the dislocation in this case is dependent only on the deformation of the lattice [14]. In a follow-up work, Bonch-Bruyevich studied the features of energy spectra of multielectron systems in semiconductors and particularly the effects caused by the interactions of current carriers [15].

In an investigation of the energy spectrum of free current carriers Bonch-Bruyevich and A. G. Mironov showed that the influence of impurities does not lead only to simple changes in spectral parameters but even alters the law of dispersion [16]. Related to this study was a paper by Yu. V. Gulyayev of the institute of Radio Engineering and Electronics, Academy of Sciences USSR, who on the basis of general considerations regarding the structure of the energy spectrum of current carriers in semiconductors with dislocations derived a formula by which the rate of filling of dislocations can be found as a function of temperature and the Fermi level in the low temperature range [17]. A general review of present knowledge of the crystal processes connected with dislocations in semiconductors was given by Ye. Yu. Kokorish and N. N. Sheftal', who compared the work in the USSR, the United States, the United Kingdom, and France in this field [18].

At the International Conference on Photoconductivity in New York in August 1961, S. M. Ryvkin of the Ioffe Institute in Leningrad presented a paper on the kinetics of impurity photoconductivity in crystals containing only one type of local levels [19].

^{*} This study may carry implications when viewed against the following remark made by N. N. Semenov with regard to the prospects of large-scale direct conversion of solar energy into electric power: "Solar energy has many advantages, except for the fact that it is so widely dispersed and has to be collected over huge areas. The only feasible way of collecting it would apparently be to cover the surface areas with a layer of light-sensitive liquid or water emulsion, with a thin plastic film on top. A central plant would isolate the high-energy product and use it in electric elements, resembling fuel elements, with almost 100% efficiency." (Semenov, N. N. Science and social progress. USSR, Dec 1961, 42-44)

In this theoretical study he showed that the excitation in impurity levels along with the thermal generation of carriers gives a linear response to light intensity except at high levels where saturation occurs as a result of impurity level exhaustion. Rise and decay time characteristics were derived and used to interpret data for various semiconductor materials.

Impurity photoconductivity was also the subject of a major work presented by S. M. Ryvkin and a team of leading solid state physicists at the Ioffe Institute in a series of seven papers. In two of the papers the general laws of extrinsic monopolar photoconductivity as dependent on the presence of one depth of impurity levels in the forbidden region were examined in detail and explanations offered of the processes of generation, capture, and adhesion of carriers. [20, 21]. The authors demonstrated that study of the kinetics of extrinsic photoconductivity offers a reliable means of determining a number of important impurity-center parameters; e.g., the photocapture cross section, the trapping cross section of free carriers, the band location of the impurity level in the forbidden gap, the concentration of the centers, and the rate of their filling. In a third paper the investigation was extended to semiconductors with several types of local levels [22]. In two other studies the kinetics of induced extrinsic photoconductivity in CdS and CdTe single crystals was investigated [23, 24], the occurrence of induced photoconductivity in CdSe and Sb Se, having been demonstrated by members of the same team [25]. In a sixth study, certain peculiarities of extrinsic and intrinsic photoconductivity with illumination of a sample of copper-doped germanium were attributed to a secondary process of the recharging of levels [26]. Finally, a method of longwave photoelectric sounding of local levels was offered along with quantitative results obtained by its application to the investigation of the behavior of nonequilibrium carriers at the local levels in Ge, Si, and CdTe. [27].

The effects of impurities and dislocations in semiconductors appear to be the principal field of basic research at the Ioffe Institute where, in addition to Ryvkin, the following names appear in connection with studies in this area: F. M. Berkovskiy, O. V. Yemel'yanenko, A. P. Komar, D. P. Lukirskiy, V. I. Myakota, and V. P. Savchenko [28, 29, 30, 31, 32]. At Moscow State University, V. A. Chapnin, in addition to Bonch-Bruyevich and V. B. Glasko, has investigated the problem of impurities and dislocations, which has also been studied by L. S. Milevskiy at the Moscow Metallurgical Institute. [33, 34]. The important work of V. S. Vavilov, the expert on silicon solar cells at the Lebedev Institute, will be discussed in Section II of this report.

Problems of recombination processes are the chief domain of recent investigations by A. V. Rzhanov of the Physics Institute Imeni P. N. Lebedev. With I. A. Arkhipova, Rzhanov conducted a study of the dependence of surface recombination velocity on the surface potential at various injection levels [35]. The results of the measurements were found to agree with theoretical calculations, showing that at the injection level which could be obtained with photoelectric excitation

of current carriers a shift of the curve of the dependence of surface recombination on the surface potential should be observed. experimental results also gave evidence that certain levels.of different energetic positions contribute to surface recombination. another study Rzhanov considered recombination statistics on the assumption that charge carriers are captured from the bands by the excited states of a recombination center [36]. He obtained a general expression for the steady-state recombination rate when the concentration of recombination centers is small and the excess hole and electron concentrations are equal. This general relationship becomes simpler for small injection levels, taking the form of the usual Shockley-Read expression when certain inequalities are satisfied. These inequalities are tantamount to the conditions under which the lifetimes of current carriers in the excited levels of the recombination center can be neglected in comparison with the time for thermal ejection or capture of a carrier of an opposite type. Calculations carried out for the case of germanium illustrate that it is quite possible for these conditions not to be satisfied. This research was extended by Rzhanov to the case of surface recombination. The extra terms in the relation for the rate of surface recombination connected with internal transitions from excited levels to the ground state made it possible to explain the temperature dependence of capture cross section and surface recombination rate, and the change in surface recombination on adsorption of certain atoms.

S. V. Bogdanov and B. D. Kopylovskiy of the Lebedev Institute showed that the effective lifetimes of nonequilibrium current carriers depend on the spectral composition of the exciting light [38]. The results obtained were suggested to be of universal character.

An important contribution to the understanding of defect properties was made by Subashiyev, who studied the increase of carrier recombination caused by the accumulation of structural defects and impurities in narrow regions of the material [39]. Volt-ampere characteristics of such regions adjacent to p-n junctions were investigated, and it was demonstrated that the dark-current value can be calculated by the use of the functions of hole and electron collection when the function of pair generation by light is arbitrary. To account for the effect of the increased recombination layer the function of hole collection was computed, and the value of the current could thus be found.

In a follow-up paper, Subashiyev on the basis of the function of hole collection from the region of the p-n junction derived an expression for the case when all parameters of this region with the exception of the hole diffusion length L are constants and the variable L is represented by a steplike curve [40]. In terms of this expression he analyzed the effect of the increased recombination layer on the dark and light characterisitics of the p-n junction and demonstrated that such a layer can generate anomalously high saturation currents in p-n junctions.

In addition to the investigative procedure referred to above, the following new methods for the computation of semiconductors were discussed in the literature reviewed: calculation of the forbidden gap in A^{III}BV type semiconductors [41]; determination of semiconductor parameters by means of the photomagnetic effect compensated by photoconductivity [42]; and photoelectric sensitivity spectra of semiconductors determined by various means [43].

II. MATERIALS

Silicon

In 1958, in a paper describing the silicon solar batteries on Sputnik III, V. S. Vavilov, A. P. Landsman, and V. K. Subashiyev stated: "Considering the totality of its properties, silicon appears to be an ideal material for semiconductor-type converters of solar energy, and one can assert in all confidence that in the coming years the basic efforts of physicists and engineers in this field will be directed toward the investigation and improvement expressly of silicon instruments." [7]. This statement may be compared with that of M. B. Prince: "Silicon with a room temperature energy gap of 1.08 ev is ideally suitable as a material for solar energy converters" [44]. Subashiyev's statement explains the fact that out of the 161 investigators whose studies were reviewed for this report, 54 dealt with silicon, many of them exclusively or almost exclusively. Among these silicon researchers, 11 showed affiliation with the Leningrad Institute of Semiconductors, 9 with the Ioffe Institute in Leningrad, and 8 with the Lebedev Physics Institute in Moscow, the remaining 26 being dispersed in 9 other institutes or universities.

Within the framework of their studies on extrinsic processes in semiconductors, the members of the Ryvkin team at the Ioffe Institute presented the results, in two papers, of experiments on silicon (and germanium), particularly their measurements of the sensitivity of gold-alloyed Si photocells in the impurity excitation region [45, 46]. They also measured, in gold-alloyed Si, the acceptor or donor levels pertaining to one structural defect in the forbidden gap. At the Lebedev Institute in Moscow, E. L. Nolle and G. N. Galkin, both noted for their Si research and the latter a specialist on Si photocells, investigated the center of carrier generation created by heat treatment in diffusion-type p-n junctions in the region of the space charge They demonstrated that in this type of junction, the currents ' produced by heat generation in the region of the space charge may be related to electron transition across the acceptor level of gold atoms located in the vicinity of the center of the forbidden gap. In collaboration with Vavilov, Nolle and Galkin presented in another work the results of their research on carrier lifetimes in a wide range of injection levels in heat-treated Si [48]. The aim of the study was to determine the location and explain the nature of the recombination levels created by heat treatment in the forbidden gap. It was shown that at temperatures above 1200°C two donor-type recombination levels appear at 0.1-0.2 and 0.35-0.002 ev above the valence band. A connection between the 0.35-ev level and the presence of gold atoms was held probable, while it was suggested that the 0.1-0.2 level might be related to dislocations, although its nature appeared less clear.

Vavilov's principal field of research seems to be various effects of irradiation of silicon by neutrons and electrons. With M. V. Chukichev of the Moscow Institute of Chemical Technology imeni

Mendeleyev he studied the occurrence of lattice defects under the influence of thermal neutrons captured by Si nuclei during irradiation of Si single crystals in a nuclear reactor [49]. It was shown that in 1 cm 5 of Si, 100 incident thermal neutrons bring about nearly 20 atom displacements and that the elimination of 4.5 conductivity electrons corresponds to the same number of neutrons captured. Studies of the influence of fast-neutron irradiation of Si on photoconductivity were reported in two papers presented by Vavilov in collaboration with A. F. Plotnikov and with Plotnikov and L. S. Smirnov, all of the Lebedev Institute [50, 51]. In cooperation with I. V. Smirnov and V. A. Chapchin, he also investigated the changes caused by the bombardment of lithium-doped Si with fast electrons in a study related to the problem of radiation resistivity of semiconductors [33]. With V. M. Malovetskaya and G. N. Galkin of the Lebedev Institute, Vavilov determined the energy levels, the concentration of defects. and the carrier concentration in electron-irradiated p-type Si with a high oxygen content, and in a follow-up paper the same team, including Plotnikov, compared the computations of the energy of thermal and photionizations, taking into account the recently discovered difference in stability with regard to annealing of two adjoining energy level centers formed by the irradiation of the sample with fast electrons [52].

Independently of the work of Vavilov and his collaborators in Moscow, four members of the Ryvkin team at the Ioffe Institute in Leningrad — N. A. Vitovskiy, D. F. Lukirskiy, T. V. Mashovets, and V. I. Myakota — succeeded in determining the complete scheme of electron-irradiated Si by investigating only the temperature dependence of the Hall effect and conductivity [see Fig. 1] [32].

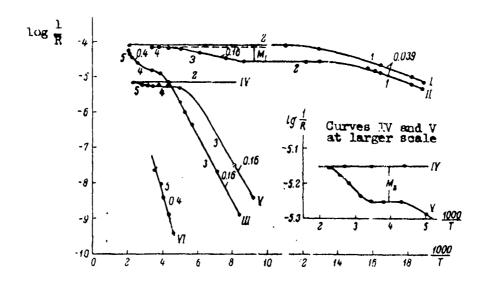


Fig. 1. Temperature dependence of the Hall coefficient for n-type Si irradiated with electrons

Their experiments on p- and n-silicon irradiated with 2-mev electrons in the linear accelerator at the Physicotechnical Institute, Academy of Sciences USSR, showed that besides the three energy levels discovered previously in irradiated Si a fourth level occurs at 0.15 ev above the valence band. Evidence was obtained that the four levels consist of one donor pair and one acceptor pair, each pertaining to one center. The cross section of the production of defects to which the levels are related was also determined.

The phenomenon of significant shortening of minoritycarrier lifetimes by prolonged heating of Si at high temperatures was studied by M. I. Iglitsyn and V. N. Mordkovich, who advanced the theory that 1) the impurities formerly fixed at the dislocations, once set free play the part of recombination centers, and 2) the dislocations, on the other hand, once cleared of impurities participate in the recombination processes [54]. To prove this hypothesis, they diffused copper onto Si samples. Examination by means of infrared microphotography showed that with heating to 900°C the diffusion brought about the filling up of dislocations; thus, the copper atoms were able to neutralize the action of the dislocations as recombination centers, causing the lengthening of carrier lifetime. However, this occurred only when the thermal diffusion lasted not more than 1.5 hrs; beyond this limit a second, simultaneous, much slower process prevailed — the penetration of the copper into the bulk of the silicon, resulting in an increase in the number of recombination centers and, consequently, shorter lifetimes.

The problem of the influence on carrier lifetime of impurity atmospheres connected with dislocations was also the subject of an independent study by L. S. Milevskiy of the Institute of Metallurgy imeni A. A. Baykov in Moscow [34]. Using copper-doped Si samples, Milevskiy showed that the normal process of lifetime extension ends after 20 to 30-min annealing at 750°C. The stability reached after such treatment was conserved after cooling but could be destroyed, with considerable shortening of lifetime, by reheating the samples to approximately 500°C, cooling, and aging at 30 to 50°C. These observations were attributed to 1) the displacement of some parts of the dislocations during the reheating and 2) an increase in recombinational effectiveness of dislocations during the process of aging.

In 1960, at the Institute of Semiconductors, Academy of Sciences USSR, a research team led by solar cell expert V. K. Subashiyev announced that the distribution of phosphorus diffused into p-type Si does not comply with Fick's second law [55]. The real depth of the p-n junction obtained by phosphorus diffusion appeared to be approximately half as large as the depth calculated. It was suggested that either the disintegration of the subsurface layer or the dependence of the diffusion coefficient on the phosphorus concentration might be responsible for this discrepancy. The effects on the light absorption of doping silicon heavily with boron up to a concentration of $\sim 10^{20}\,\mathrm{cm}^{-3}$ were the object of an important study

presented by Subashiyev in collaboration with Dubrovskiy [56]. The authors found that such doping displaces insignificantly the absorption edge into the region of higher energies. The smallness of the effect indicates the nonparabolism of the Si valence zone.

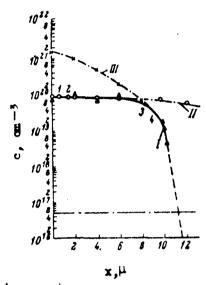


Fig. 2. Distribution of boron atoms in doped Si layer

I - experimental curve; II - curve computed from Fick's equation (along points 1 and 2), c₀=9.2·10¹⁹ cm⁻³; III - curve computed from Fick's equation (along points 3 and 4), c₀=1.5·10²¹ cm⁻³

In view of its importance for the construction of solar batteries, the impurity diffusion technique was studied by A. K. Zaytseva and A. Ya. Gliberman, also of the Institute of Semiconductors, who measured phosphorus diffusion in p-type Si and boron diffusion in n-type Si [57]. A method similar to that described by Subashiyev and his associates was used, i.e., thin layers of the sample were etched off and, layer by layer, such data as maximum power, resistance, open-circuit voltage, and shortcircuit current were noted. The experiments showed that the distribution of boron (as well as of phosphorus) atoms in the alloyed region did not conform to Fick's second law [see Fig. 2]. Thus, Subashiyev's discovery was not only confirmed but seemed to apply also to impurity diffusion in n-type Si. The concentration of the diffused impurities down to the immediate vicinity of the junction was found to be almost uniform, falling even more steeply to zero than had been the case in the Subashiyev study [10 Juj.]. No firm explanation was offered for the phenomenon observed; it was noted only that some aspects of the thermal

diffusion process in Si might play a role which cannot be elucidated by the general theory of diffusion.

In a study by two other researchers at the Leningrad Institute of Semiconductors, B. I. Boltaks and N. N. Matveyeva, a tentative explanation was offered of the unusual diffusion concentration curve in Si [58]. They investigated the diffusion of impurities in Si with the use of $P^{3/2}$ isotopes, and their experiments on the diffusion of phosphorus in p-type Si once more confirmed the findings of the Subashiyev team [see Fig. 4]. Some evidence was obtained that the phenomenon may be simply the result of evaporation of phosphorus during the diffusion process. However, preliminary experiments performed by Boltaks and Matveyeva on n-type Si yielded results which

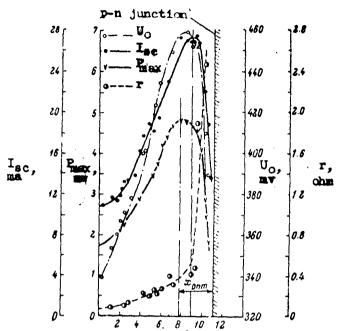


Fig. 3. Change of electrical parameters of an Si photoconverter as the thickness of the doped layer is reduced.

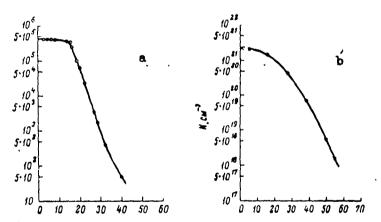


Fig. 4. Distribution of phosphorus in silicon with annealing in a - nonsaturated and b - saturated phosphorus vapor

appeared to contradict those obtained by Zaytseva and Gliberman with boron: concentration curves plotted for both n- and p-type Si under identical conditions of diffusion annealing showed for n-type Si close conformity with Fick's second law. The presence of a much denser exide film on n-type Si was suggested as an explanation. Further elucidation of the same problem was received from the Institute of Physics of the Bulgarian Academy of Sciences in Sofia where researchers D. N. Mikhaylova and I. D. Kasabov obtained curves for the distribution of various concentrations of phosphorus diffused into p-type Si [59]. At higher concentrations, these curves were similar to those reported by Boltaks and Matveyeva and showed once more that Fick's second law does not hold, at least under the conditions described.

In 1958 Vavilov, Galkin, and Malovetskaya presented preliminary results of their experiments on increasing the efficiency of Siphotovoltaic cells by the use of light concentrators [60]. They showed that if the temperature of the cell is maintained at approximately 25°C a threefold increase in electric power can be obtained by a sixfold concentration of light. The same year Vavilov, Landsman, and Subashiyev drew attention to the possibility of using solar light concentrations on orientable artificial earth satellites [7].

Experiments, apparently on quite a large scale, on the functioning of Si photoelements under intensified light concentration were begun in 1959 by the Heliotechnical Laboratory of the Power Engineering Institute imeni G. M. Krzhizhanovskiy, Academy of Sciences USSR. By 1960 the Laboratory had accumulated sufficient data to confirm the great possibilities offered by light concentrators. It was established that in certain cases the output of the converter could be increased up to 20-30 times with a 100- to 150-fold increase in light intensity [61]. More recent investigations performed at the same laboratory on Si photoelements with an efficiency of 3 to 10% established a number of parameters to guide constructors of concentratorequipped instruments [62]. A first series of tests showed that if the cells were not cooled the buildup of temperature in the semiconductor material reached 110°C at a light concentration of ~ 0.4 w/cm² and went up to 200°C with further increase in illumination. The output of the majority of the samples was doubled when the incident light was intensified from the natural level of \sim 0.06 w/cm² to \sim 0.3-0.5 w/cm². At still higher light intensities the output began to decrease. Only three but of nine Si test elements yielded a four to fivefold increase in Illumination of a sample with $\sim 2 \text{ w/cm}^2$ brought about a drop in the output power; when the temperature reached 235°C the solder began to melt. Fig. 5 shows the results of a second series of experiments performed with nine different Si photocells cooled with running water to a temperature below 55°C at a light concentration of up to 15 w/cm2. As can be seen, the output of all the elements rose rapidly in the illumation range of 4 to 5 w/cm² (4 w/cm² corresponding to a 70-fold light concentration). Further increase in illumination appeared to be ineffective. However, if the element worked at saturation at an illumination level slightly above 5 w/cm2 its output reached stability and became independent of oscillations in light intensity. Only one of the nine water-cooled Si photocells gave a 19-fold increase in output, the rest yielded 5 to 8 times their original power.

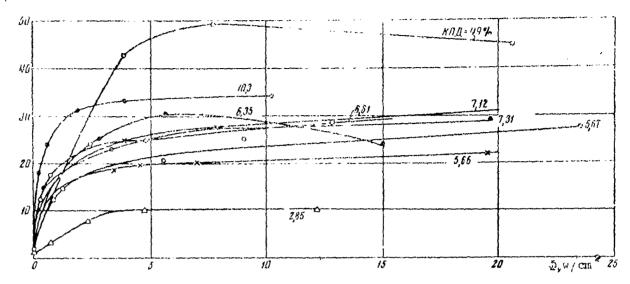


Fig. 5. Dependence of power output of water-cooled photoelements on light intensity

By 1962 the research on light concentrators had been moved to the new scientific center in Uzbekistan, where A. P. Landsman, the solar cell expert from the Leningrad Institute of Semiconductors, joined a team of researchers at the Physicotechnical Institute of the Uzbek Academy of Sciences. In a paper published in Tashkent, Landsman and five associates presented the results of their experiments with a parabolic mirror for focusing light on an Si photobattery with a working surface of 288 cm² [63]. With a sevenfold increase in the light flux, power output was raised 3 to 4 times, and the hope was expressed that an eight to tenfold increase might be obtained after the cooling system had been improved and uniform illumination of the entire battery surface had been secured.

Other quantitative studies of the dependence of the photovoltaic cell output on light intensities were made in Tashkent by P. I. Knigin and L. A. Dubrovskiy of the Physicotechnical Institute of the Uzbek Academy of Sciences [64, 65]. Their analysis of the volt-ampere characteristics of photoelements at illuminations up to 100 times higher than solar intensity was found to be in agreement with experiments performed on a water-cooled Si converter with a diffused phosphorus p-n junction and a light concentrator in the form of a diaphragm-controlled lens. Fig. 6 shows the dependence of the optimum power Popt and the optimum efficiency Topt on the energy of the incident light R concentrated up to 7 w/cm². Fig. shows the same dependence of the optimum current Lopt and the optimum resistance Ropt of the photocell. These findings confirmed

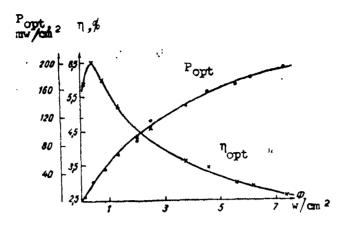


Fig. 6. Dependence of optimum power output and efficiency on light intensity

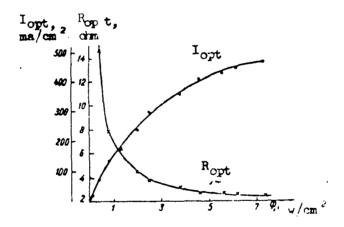


Fig. 7. Dependence of optimum current and optimum resistance on light intensity

the observations of Vavilov, Baum, and others who had reported a deviation from linearity of the light-intensity/short-circuit-current dependence. Knigin and Dubrovskiy explained the deviation by the distributed character of the surface layer resistance which causes the potential difference V between the base and the edge of the photoelement on the opposite side of the current-carrying contact to become at higher light intensities almost independent of further increase in illumination:

Light intensity, w/cm	v_{o}	I_{SC}
0.37	90	54
0.75	160	101
1.25	285	170
1.95	430	262
2.80	555	358
4.00	610	450
4.9	620	505
5.8	628	557
6.4	629	585
7.5	630	637

A variety of experimental Si solar batteries equipped with reflectors was tested in the vicinity of Tashkent by G. S. Daletskiy and N. V. Shavrin with the aim of determining certain basic structural parameters [66]. Experiments with a square battery, to which adjustable square metallic reflectors were attached on each side, gave the following output amplification coefficients (obtained by dividing the output of the reflector-equipped battery by that of a battery without reflectors): battery with one reflector, 1.23; with two reflectors, 1.43; with three reflectors, 1.65; and with four reflectors, 1.82. The highest overall efficiency for nonautomatically orientable batteries was obtained at a reflector angle of 30°. The account of these experiments also includes some information on Si photovoltaic instruments in actual use in the USSR, and photographs are given of units used for charging of storage batteries and for supplying power to electronic instruments or to electric clocks. The following data are given on certain standardized Si photovoltaic converters which produce 0.4 v at a light intensity of 100 mw/cm and a temperature of 30°C:

Type	Size, mm	Working surface, cm ²	Average effi- ciency,%	output current, ma	output, mv
ФКЦ-2 ФКЦ-3 ФКЦ-4 ФКЦ-5	10x10 10x15 10x20 10x30	0.85 1.275 1.70 2.40	8 8 8	18 27 36 50	7.2 10.8 14.4 20.0

Like their Western counterparts, the Russian photovoltaic cell researchers are greatly concerned with the high price of Si monocrystals. One solution is seen in the development of more efficient polycrystalline solar cells, a task which A. P. Landsman and his associates at the Leningrad Institute of Semiconductors seem to have dealt with since 1960, if not earlier [67]. In a review of their research, Landsman, A. Ya. Gliberman, and A. K. Zaytseva provided data on many features of their investigations, particularly the effects of orientation, order and size of grains, and the "jumps" in resistivity caused by the boundary regions between the grains [68]. They reached the general conclusion that although polycrystalline material is less efficient than single crystals because it yields slightly lower open-circuit voltage and short-circuit current, its overall characteristics differ little from those of single-crystal elements. A maximum output of 5 to 6 mw/cm² was obtained per unit of working surface at solar illumination, with the cost of a 1-w battery being 2 to 3 times less than if it had been made of singlecrystal Si.

Other attempts to reduce the cost of Si solar patteries included tests of cells with working surfaces on both sides of the photoelement, one side being illuminated with direct light, the other with light reflected by a mirror [see Fig. 8] [69].

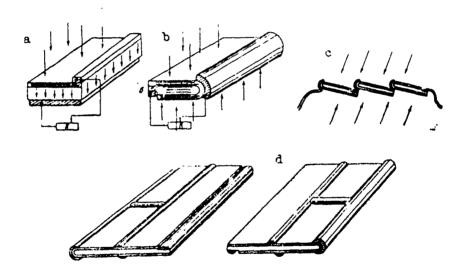


Fig. 8. Construction, wire leads, and arrangement of photovoltaic energy converters

a - one-sided; b,c,d - two-sided

Since such instruments showed an output increase of only 1.2 to 1.3 compared with single-sided cells, they were found to be practical only in some large installations and only with the use of Si having a resistivity \leq 0.1 ohm/cm. Improvements were also sought by experimenting with various contact materials [70]. The best results were obtained by deposition of Pd, with Rh and Ni ranking second and third [see Fig. 9]. Rhenium showed poor adherence to Si, while Ni had a much higher series resistance with the photoelement (2.86) than Pd (0.57).

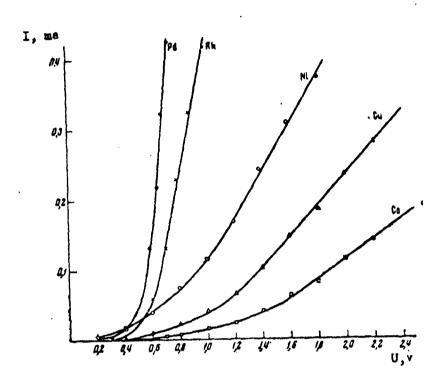


Fig. y. Dark characteristics of a photoelement with contact of various metals

Cadmium Telluride

Four years before Soviet scientists Vavilov, Landsman, and Subashiyev went on record naming silicon "the ideal material for semiconductor-type converters of solar energy," [7] the high hopes for Si in the West were shaken by Cummerow's statement that the optimum material should have an energy gap of 2 ev and not the 1.1 ev attributed to silicon [71]. Rittner took up the problem and confirmed that the Si Eq lies well below the optimum level, which according to his computation should be 1.5 to 1.6 ev [72]. Prince disagreed, maintaining that the optimum occurs at approximately 1.3 ev and that the difference between the efficiency of Si and the ideal material therefore is very small [44]. He was,

however, disproved by Loferski of the RCA Laboratories who presented an extensive study of conditions governing the choice of the optimum semiconductor for photovoltaic solar energy conversion [73]. The conclusion to be drawn from his calculation was that when all the pertinent interactions are considered, the efficiencies of semiconductors for which 1.1 ev < E_G < 1.6 are higher than the efficiency of Si and that their advantages are even more pronounced for the conversion of solar energy outside the atmosphere.

Highest on the list of materials within the range of optimum semiconductors computed by Rittner and Loferski was cadmium telluride, an intermetallic compound which had been little studied. Loferski's paper appeared in July 1956 and six months later, in January 1957, four researchers of the Leningrad Institute of Semiconductors, among them solar cell expert Yu. P. Maslakovets, submitted for publication a "preliminary report" on their experiments with CdTe as material for photovoltaic light converters [74]. They used n-type CdTe wafers consisting of 3 to 5 crystals, on which p-layers were formed by the diffusion of group I elements. At a solar light intensity of 30 mw/cm² they obtained a photoemf of 500 mw and a short-circuit current of 2 ma/cm². Although the efficiency of these first cells was only about 2%, the investigators stressed that this was far below what eventually could be obtained from the new material. It is worth noting that the only references quoted in this brief communication were the papers by Rittner and Loferski.

For twenty-seven months after this preliminary report had been submitted for publication the names of Maslakovets and his three associates could not be traced in Soviet science journals. However, in April 1959 the team submitted three extensive papers, published simultaneously in January 1960, which covered most of the basic facets of CiTe as material for photovoltaic solar energy converters and which were obviously based on a wealth of experiments carried out over a long period of time. Remarks in these papers make it clear that a fifth researcher, G. B. Dubrovskiy, was also working on CdTe at the Institute and that the team was benefiting from the help of one of the Institute's prominent theoreticians, B. Ya. Moizhes.

The first of the above papers contains a general description of experimental CdTe photoelements produced by direct melting of Cd and Te with subsequent crystal growing from the melt [75]. The energy gap was found to be 1.38 to 1.48 ev, close to the values which had been reported earlier in Western journals. Indium and gallium were used to obtain n-type material; p-type was obtained by diffusion of Au, Li, Sb, and Ag. Both p-n and n-p junctions were tested, the n-type with a carrier concentration of the order of 10¹⁷ cm³ giving better results. The junctions were produced by deposition of semitransparent layers of metal onto the polished and etched plates cut out of the single crystal, with subsequent heat treatment. The experiments confirmed that CdTe photocells could be used in solar batteries. The optical properties of the

cells [see Fig. 10] were similiar to those made of Si, though their efficiency reached only about 4%*, mainly because the deposited layers transmitted only about 50% of the incident light, and the quantum yield was further reduced by the incomplete separation of the electron-hole pairs. The general nature of the load characteristics was not affected by a rise from room temperature to 101°C, but the emf showed a decrease close to that observed in Si photocells.

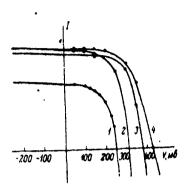


Fig. 10. Volt-ampere characteristics of a CdTe photoelement at various light intensities.

Number of curve	E, lx	Ι _{sc} , μα	v_{oc}	Filling coef- ficient	R _{opt} , cm ² ,kohm
1 2	. 4	26	245	0.59	334
	30	9.6	32 5	0.62	68
3	300	92	375	0.67	8
4	3000	950	430	1.59	0.72

^{*}At the ARS Space Power Systems Conference in Santa Monica September 27-30, 1960, Loferski quoted this paper, stating that the efficiency of 4% obtained from CdTe by the Russians was the highest ever achieved (Loferski J. J. The photovoltaic effect and solar energy conversion. IN: Energy conversion for space power. New York, 1961, 221-230.)

The second paper was devoted in its entirety to a detailed theoretical and experimental study of the properties of CdTe p-n junctions [76]. The light and dark characteristics of two photoelements are shown in Fig. 11. Volt-ampere characteristics for

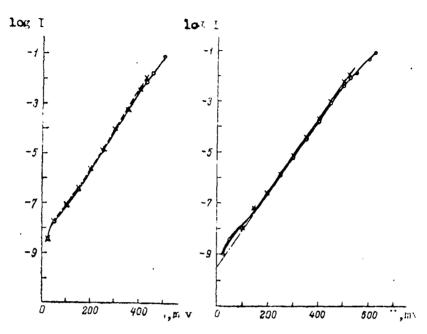


Fig. 11. Dark and light characteristics of two CdTe photoeiements

various samples were established and the basic parameters computed. The study showed that the short lifetimes of carriers in both p-type and n-type CdTe were responsible for the high saturation current of the junctions, precluding higher efficiencies. Another reason why an efficiency higher than 4% could not be obtained was the presence of the semitransparent metallic electrode which transmitted only half of the incident light. It was suggested that further research might be directed toward increasing carrier lifetime, the caution being expressed, however, that this might bring up the price of the photocells because of additional complexities in the preparation of the material.

The fact that CdTe belongs to a group of compounds which are affected more than many others by physicochemical surface conditions prompted a special study of CdTe surface layers, the preliminary results of which were presented by the same team in the third paper [77]. The experiments showed that if n-type CdTe is exposed to air for a sufficiently long time, a p-layer with its rectifying characteristics forms on the surface. Conversely, with prolonged exposure to air of samples of p-type material, the formation of conducting layers was observed at the surface of the single crystals. Heating of the specimens resulted in a particularly sharp lowering of resistance. X-ray investigations of the material did not reveal

any change in the composition of CdTe, and the conclusion was drawn that the surface of both p-type and n-type CdTe must be enriched with acceptor impurities. This hypothesis was verified in experiments which established that the acceptor impurity activation energy lies within 0.2 to 0.5 ev. On the strength of further experiments the hole conductivity in CdTe surface layers was tentatively explained by the presence of vacant Cd sites or the removal of donor impurities from the surface. The authors regarded atmospheric oxygen as the probable principal factor in the formation of surface layers on CdTe, but suggested that the problem required further studies.

After the publication of the above papers, nothing was heard from Maslakovets and two of his associates. Only the name of Naumov reappeared, once, two years later as coauthor of an extremely short communication [78]. A full translation of this note follows.

Efficiency of the conversion of the energy of direct solar radiation into electric energy by means of a CdTe photoelement.

G. P. Naturov and G. V. Nikolayeva

Photoelements of CdTe were the subject of communication (1). At present, as a result of further developments in the technology of preparing p-n junctions in CdTe, the efficiency of photoelements used in direct solar light has been successfully increased.

Efficiency measurements were conducted this year in mid-April at noon. The intensity of the incident solar radiation angle of ~ 0°, was 77.2 mw/cm². Exposed to such light, a photoelement with a surface of ~ 1 cm² yielded a short-circuit current of 9.8 ma/cm². The open-circuit voltage was 0.75 v. The photoelement developed the highest useful power at a voltage of 0.6 v and a current of 7.8 ma/cm², corresponding to a load resistance of 77 ohm-cm². The useful electric power was 4.65 mw/cm². Consequently, the efficiency of such a photoelement at direct solar light amounts to 6%. The filling coefficient of the load characteristic at such an intensity of incident solar radiation was 0.63.

References

(1) Yu. A. Vodakov, G. A. Lomakina, G. P. Naumov, and Yu. P. Maslakovets. FTT, 2, 3, 1960; FTT, 2, 15, 1960.

Institute of Semiconductors
Academy of Sciences USSR
Leningrad

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If the workers of the Liningrad Institute of Semiconductors had succeeded in obtaining 6% efficiency of CdTe photoelements without excessively raising the cost of preparing this relatively inexpensive material, they would have taken as important step toward realization of their ambitious plans for large scale solar energy conversion. Naumov's and Nikolayeva's communication is in this respect noncommittal. However, in this connection, the subsequent extension of Soviet research on this particular compound may be of some significance.

Even before the note quoted above appeared, other properties of CdTe not covered by the research of the Maslakovets team had been investigated by Soviet physicists. Dubrovskiy, who in the mid-fifties worked with Maslakovets on Si photoelements [79] at the "atter's request turned as early as 1959 to the study of the optical properties of CdTe. In a first series of experiments he performed detailed measurements of the spectral sensitivity of a number of CdTe photoelements in order to establish the effect of shortwave light on the multiplication of electrons [80]. The measurements showed a significant drop in the values of $Q \cdot \alpha$ — the product of the quantum yield of the material Q and the collection coefficient α — with an increase in photon energy in the range 2.5 to 3.5 ev.

Taking into account that the quantum yield of the material is constant within the limits $E_G < hv < 2 E_G$, this indicates a reduction of the collection coef-

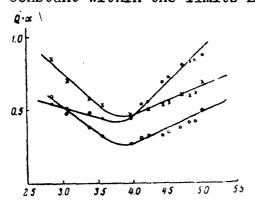


Fig. 12. Dependence of $\mathbf{Q} \cdot \boldsymbol{\alpha}$ on the energy of incident photons of three CdIe samples

ficient in the shortwave region of the spectrum. Contrary to the expectation that with further increase in photon energy the collection coefficient would continue to decrease, the experiments showed a fairly rapid increase. This rise of the Q.a value in the range 3.5 to 5.0 ev was explained by the increase in the quantum yield of the material, i.e., as an effect connected with the multiplication of electrons or holes at carrier energies surpassing the width of the forbidden gap of CdTe. The surplus of energy of majority carriers

necessary for producing impact ionization was found to be approximately 2 ev.

In a follow-up paper, Eubrovskiy presented the absorption and reflection coefficients of CdTe in the 0.4 to 6.0 μ region of the spectrum [81]. The effects of photon energy on the absorption coefficient are shown in Fig. 13. He also took up the observations of Maslakovets and the latter's associates regarding peculiarities in the surface properties of the material, confirming that a lengthy

exposure to air causes the formation of a surface film which distorts the absorption curve.

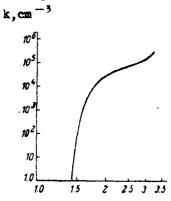


Fig. 13. Dependence of the light absorption coefficient k on the energy of the incident photons hy for CaTe samples

Independently of Dubrovskiy's work, M. V. Kot and Yu. Ye. Maronchuk of Kishinev State University investigated the optical characteristics of CdTe, concentrating on the properties of thin layers of the material [82]. They showed that the absorption coefficient increases in the infrared region for layers < 0.5 μ and that the electrical conductivity of such layers is much higher han that of thicker ones. No appreciable shifts in longwave cutoffs with changes in sample thickness were observed - the absorption coefficients for all samples measured corresponded to wavelengths of 8700 to 8800 A or photon energies of 1.4 to 1.42 ev, findings which agree with data for CdTe monocrystals.

Annealing had no effect on the wavelengths, though it increased the granularity of the material, a possible cause of the reduction observed in the amount of transmitted longwave light. Stoichiometric samples showed much better characteristics than those with an excess of Te. Samples with an excess of Cd were strong absorbents. However, after vacuum annealing at 350°C, CdTe thin layers with an excess of either Cd or Te showed transmission characteristics close to those of stoichiometric samples. It may be noted that two members of the Drogobych Pedagogical Institute more recently called attention to the marked increase in photocurrent, along with an increase in dark current, which they had obtained from CdTe thin layers activated by mercury [83].

A major contribution to the understanding of certain peculiarities of GdTe was made by S. A. Semiletov of the Enstitute of Crystallography, Academy of Sciences USSR, in Moscow, who offered an explanation for the unusually high photovoltage which shows across the ends of CdTe vacuum-evaporated thin films [84]. The phenomenon was discovered in 1957 by Pensak of the RCA [85], and the electrical properties of thin films were described by Pensak's collaborator, Goldstein [86]. The American researchers had obtained a value of 100 v/cm and had established that the presence of the effect and its magnitude depend on the angle at which the CdTe vapor is deposited onto the substrate, i.e., that the high photovoltage appears only if in deposition of the film the molecular beam is directed at a slanting angle to the substrate. Since the photovoltage of a single junction is limited by the band gap of the material (in this case, 1.45 ev) Fensak and Goldstein concluded that the effect must be caused by a multiple gap phenomenon produced by a hitherto unknown crystallographic ordering process.

In his paper Semiletov stated that the crystallographic ordering process of CdTe had, in fact, been known before the American discovery of the high photovoltage effect and that he himself had described it in 1955 and 1956 [87, 88]. Semiletov added: "Pensak apparently ignored these works and was therefore unable to suggest any mechanism producing the high voltage photoemf in thin films of CdTe." According to Semiletov's electronographic investigations, this mechanism is a peculiarity of the crystallographic arrangement in CdTe and consists in two simultaneously present, orderly spaced modifications—a cubic and a hexagonal one. The mutual orientation of the crystallites is: face [0001] hex || [111] cub and direction [1120] hex || [110] cub [see Fig. 14]. The high voltage photoemf is

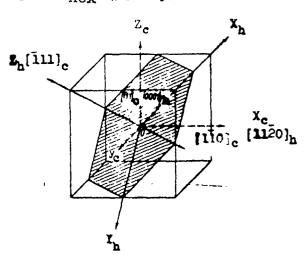


Fig. 14. Relative position of cubic and hexagonal crystallites in a CdTe layer

caused by the departure from the ideal regular arrangement of the atomic layers, i.e., by the defects in the packing and by the boundaries at the transitions from hexagonal to cubic packing and vice versa.

Semiletov provided the following explanation of the dependence of the high photowooltage on the vapor deposition angle and on the vector of the electric field. If the film is deposited by evaporation at an angle perpendicular to the substrate, layers horizontal to the substrate will develop, with the electric field vector taking a vertical position, and no voltage will show across the ends of the

sample. If, however, the film is deposited at a stant, the field vector will take the same position, with the photoems being proportional to the sine of the angle between the normal to the plane and the direction of the vapor stream. The occurrence of a very high emf in thin CdTe films was observed also by another investigator; in this case the governing condition was that the films were deposited on a substrate of a highly insulating material [89].

With the exception of the news item in a Lithuanian newspaper quoted earlier [4] to the effect that a team of specialists were at work early in 1961 at the Laboratory of Semisonductors of the Lithuanian Institute of Physics and Mathematics on "new semisonductor devices from thin CdTe films" for power generation and other uses, no reports have been found which indicate that CdTe solar batteries are in actual use in the Soviet Union.

Other Materials

In their evaluation of materials having the theoretically most propitious energy gap for use in photoelements, Rittner and Loferski rated gallium arsenide about as high as CdTe [72, 73]. Also, at the time when the highest efficiency of CdTe experimental cells did not attain 4%. GaAs cells with an efficiency of 9% were reported by the RCA Semiconductor Products Division [90]. It was further recognized in the United States that GaAs is more immune to radiation than Si, and because it can be used at temperatures above 150°C it was singled out as a material particularly suitable for light-concentrator equipped devices [91].

In the USSR, GaAs did not until recently appear to be of great interest to Soviet solar battery experts. Kolomiyets, a leading scientist in the field, considered arsenic a "troublesome" material [92], and no paper on GaAs could be found bearing the signature of any of the specialists on the photovoltaic effect at the Institute of Semiconductors in Leningrad. Although Nasledov of the Ioffe Institute has been studying GaAs since 1957, he has given no explicit indication that he would consider this semiconductor particularly valuable for solar energy conversion. It should be noted also that Nasledov does not deal with this one material exclusively, as is the case of many experts on Si, CdTe, or CdS, and that he has devoted more of his time to InSb than to GaAs.

B. V. Tsarenkov has been Nasledov's most frequent collaborator in GaAs research since 1957, but other members of the Ioffe Institute, including Ryvkin, have joined them in various investigations. The main topics have been the properties of p-n junctions and volt-ampere characteristics [93, 94], the dependence of spectral characteristics of GaAs photoelements on the diffusion of Cd and Zn impurities and on etching [95], the spectral distribution of recombination radiation [96, 97]*, and the anomalous decrease of the resistance of n-type GaAs under the influence of a magnetic field [98] — an effect discovered, but not explained by Yemel'yanenko and Nasledov in 1958 [99]. Independent studies of GaAs were made also by workers of the Institute of Physicotechnical and Radiotechnical Measurements in Moscow, who determined the resistivity, Hall coefficient, and magnetic resistance in n-type GaAs at impurity concentrations of 1016 to 1017 cm⁻⁷ [100], and at Zhdanov University where GaAs photoemission was investigated [101, 102].

Nasledov's interest in indium antimonide dates from 1956 when, aware of the work done by Western researchers such as Madelung, Weiss, Fritzsche, and Lark-Horovitz, whom he quotes in his references, he began experimenting on samples which proved not to be pure enough

^{*} It may be noted that during this particular research Nasledov also dealt with interactions which might be connected with laser-type emission.

to yield reliable data [103]. Early in 1957, however, the laboratory which he directs at the Ioffe Institute succeeded in producing InSb of remarkable purity [104], and from then on Nasledov, in collaboration with several associates at the Institute, devoted much, if not most, of his time to InSb research, although the characteristics of this material seemed to confine the field of its application chiefly to the detection of infrared radiation. Reports on InSb bearing Nasledov's name include studies on photosensitivity [105], electric properties of p-type and n-type materials [106, 107, 108, 109], the photomagnetic effect and effects of magnetic fields [110, 111, 112, 113, 114, 115], and he behavior of current carriers. The last subject was covered in a thorough investigation of the mechanism of carrier scattering [116, 117, 118, 119], a process which Nasledov explains by free charge carriers, the acoustic oscillations of the lattice, and interactions of impurity ions. He also studied the properties of InSb-AlSb solid solutions [120, 121], while solar cell expert Koloniyets, published a paper on InSb-GaSb [122] and investigated a method of growing InSb-GaSb double crystals with the aim of obtaining a multiplegap semiconductor material [123].

Before InSb research had been taken over by the Ioffe Institute, V. P. Zhuze and I. M. Tsidil'kovskiy of the Institute of Semiconductors in 1958 published a report on their work on the magnetic field effects in InSb [124]. More recently, Tsidil'kovskiy published the results of his studies of transport phenomena in InSb [125], and this compound was also included in his investigation of electron and hole scattering in compounds of the A^{III}BV group [126]. Data on InSb were contributed by D. Kh. Amirkhanova and R. I. Bashirov of the Dagestan Branch of the Academy of Sciences USSR in Makhachkala [127, 128]; by a team at Moscow University, who experimented with InSb subjected to millimeter radiation [129]; and by N. N. Sirota and Ye. M. Gololobov, who independently of Nasledov's work on electron states, presented numerical estimates of the radii of In and Sb ions at two electron density levels. [130].

Gallium phosphide is the third semiconductor in which Nasledov has shown recent interest, although restricted by the difficulties in obtaining GaP crystals [131]. The absorption spectrum of this compound was studied earlier by Gross and his associates [132].

Soviet institutes and personnel working on cadmium sulfide can be compared in number only with those doing research on Si. Probably because of the early interest shown in this material by Academician V. Ye. Lashkarev, who in 1952 in collaboration with G. A. Fedorus discovered that the photocurrent could be photoactivated in CdS by irradiation [133] — a phenomenon he is still working on — much of the CdS research is centered in the Ukraine: in Kiyev at the Institute of Semiconductors and the Physics Institute, both of the Academy of Sciences USSR, and the State University, and in Odessa at the State University. Of 32 Soviet solid state physicists whose recent work has been exclusively or almost exclusively devoted to CdS, 18 are affiliated with these institutions.

The "anomalous" behavior of CdS under various circumstances was the main subject of study during the period reviewed for this report. Lashkarev and his associates at the Institute of Semiconductors in Kiyev published their research on photoactivation by short square pulses [134]. Other scientists in the Ukraine investigated such electrical properties of the compound as the increase in electrical conductivity as a function of time [135], the change of the sign of photoconductivity with illumination [136], the effect of a strong electric field on the growth of photocurrent and thermostimulated conductivity [137, 138], and gamma and electric conductivity. the last a comparative study [139, 140]. The Americans R. Williams and R. Bube in 1960 presented evidence that in photoelements of Lowresistance CdS with electrolytically deposited copper or other metals the phenomenon of a "surface" photoeffect occurs from the metals into the semiconductor [141]. These findings were confirmed in experiments by Paritskiy, Rogachev, and Ryvkin of the Physicotechnical Institute in Leningrad, who provided a tentative explanation of the mechanism of the process by drawing an analogy with the production of emf in the presence of an n-p junction [142]. They suggested that the metal deposited onto n-type CdS acts as if it had become a p-type semiconductor, a plausible phenomenon because the metal electrons which absorb photons with an energy higher than that of the barrier can play the part of nonequilibrium minority carriers.

The phenomenon of infrared quenching in CdS crystals, which began to occupy Soviet researchers in 1956 [143] ten years after it had been discovered in the West [144] and which according to them might help to provide an insight into the general optical properties of semiconductors, is being investigated in depth at Odessa State University by T. Ya. Sera and his associates [145, 146, 147]. Fig. 15 shows the absorption curves of two different samples, and Fig. 16 shows the effect of annealing on the spectral distribution of the photoelement.

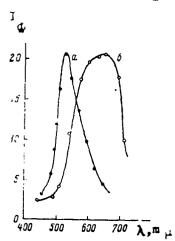


Fig. 15. Change of spectral distriution of photoconductivity of CdS
single crystals caused by crushing
and pressings as before processing
be after crushing and pressing
28.

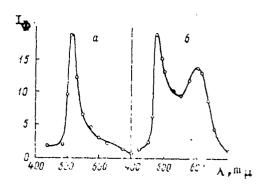


Fig. 16. Influence of annesling and tempering on the spectral distribution of the pootcourrent to (16) - Figle crystels. Photocolustivity spectrum after second their second research, to tempering

These scientists also computed and explained the optical effects of γ -irradiation of CdS samples [148]. Extensive research on other optical properties of this semiconductor is being done at Leningrad State University by Ye. F. Gross [149, 150, 151, 152, 153, 154], whose interest dates back to 1956 [155, 156] and who with B. V. Novikov in 1958 and 1959 showed the exciton structure of the CdS crystal absorption edge [157, 158]. In Kiyev, under Lashkarev's supervision, four physicists of the Institute of Semiconductors demonstrated that the sensitivity of CdS to light, x-rays, and Y-rays can be increased by the introduction of gold atomsinto the lattice [see Fig. 17 and 18] [159], while at the Physics Institute, also with

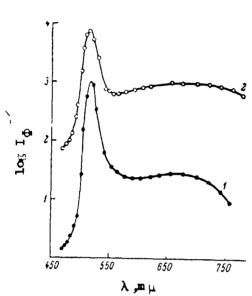


Fig. 17. Spectral distribution of photocurrent of 1 - pure and 2 - gold-doped GdS single crystals

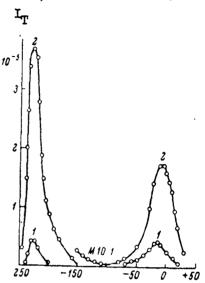


Fig. 18. Thermostimulated conductivity of 1 - pure and 2 - gold doped CdS signs or veisle

Lishkarev's help, a method for studying dislocations in CdS was devised [160]. In none of these papers, however, was a direct statement found which would indicate that CdS is in a stual use in solar batteries in the USSR.

That CdTe is not the only material in which light generates an anomalously high photoemf was demonstrated by V. M. Lyubin and G. A. Fedorova, who obtained a photoemf of 30 to 120 v from 1 to 5 μ thick antimony triselenide films return-evaporated onto glass or mice substrates [161]. As in the case of CdTe, the value of the photovoltage depended on the angle at which the molecular beam was directed to the substrate; best results were obtained at angles of 25 to 45° and a substrate temperature of approximately 300° C.

The marked interest of Soviet researchers in cadmium selective originated with the demonstration by Schwarz in the early fifties of the high photosensitivity of this material [162, 163]. Encouraged by Kolomiyets, semiconductor physicists in Leningrad started their own research, and the results of the first series of experiments [164, 165] appeared to justify the expansion of CdSe studies in Leningrad as well as other scientific centers. Ukrahian researchers took over much of the CdSe work, undoubtedly because of the similarity in the properties of CdS and CdSe discovered by Lashkarev's team in Kiyev [166]. In 1958 Lashkarev himself repeated on CdSe the photoactivation experiments he had performed on CdS six years earlier [167]. However, as in the case of GaAs and CdS, no reports have been found of the use of CdSe in photovoltaic cells. Published research indicates that the immediate Soviet aim is rather to gain knowledge of the material's electrical properties [168, 169, 170, 171], optical properties [172, 173], and crystallographic characteristics [174], and to develop methods of preparing this compound [175].

As soon as Prince in 1954 drew attention to the possibility of using aluminum antimonide in solar batteries this material was studied by the Soviet solar cell expert M. S. Sominskiy [176]. Recent literature, however, does not reflect marked interest in this compound. Two workers at the Moscow Metallurgical Institute investigated AlSb, and though they termed it "one of the materials with a future" they restricted themselves to a superficial study of its properties with tellurium, selenium, and sulfur as impurities [177]. Similarly, little mention was found of indium phosphide — a compound high on Loferski's list of materials having the most favorable energy gaps—although Nasledov, who studied the carrier lifetime of the compound, mentioned that InP may be valuable for many technical applications [168].

CONCLUSIONS

One fact which emerges clearly from the literature reviewed for this report is the emphasis among Soviet researchers upon theory, and in this respect the present survey is in full agreement with earlier findings of Conyers Herring of Bell Telephone Laboratories, who estimated (as quoted by George A. W. Boehm in the November 1961 issue of Fortune) that 60 percent of Soviet papers on solid state physics are chiefly theoretical as against only 35 percent of the American ones.

The majority of the photovoltaic cell experts in the USSR seems to be much more interested in working out general formulas to explain experimental results than in trying to solve experimentally any practical problems. Aided by rigorous mathematical training, these scientists - many of them young men judging from the fact that their names did not appear in journals published before 1959 - may well prove able to achieve their aim of replacing the present inadequate theoretical framework underlying the photovoltaic phenomena with one in better agreement with observable data. In this field the work of such men as Lashkarev, Gubanov, Subashiyev, Bonch-Bruyevich and Ryvkin should be given close attention.

While the task of reworking the photovoltaic effect theory may take time, there are reasons to expect that the heavy reliance of Soviet researchers on theoretical considerations is already paying off by allowing them to avoid certain costly mistakes; for example, they correctly chose for their sputniks the p-type-base silicon cell instead of the easier to produce but much less radiation-resistant n-type used in the cells of the US satellites.

A second salient point is that the USSR is accelerating these programs by assigning large numbers of researchers to various aspects of the same problem. The case of extrinsic photoconductivity phenomena is typical. Once it was recognized that the shortcomings of current explanations of these processes were the major stumbling block in many branches of semiconductor applications, Ryvkin, the best man in the field, was given the task of producing a more effective theoretical framework. He has gathered around him Khansevarov, Paritskiy, Berkovskiy, Arkad'yeva, Strokan, Kasymova, Yaroshetskiy and Rogachev, eight highly trained solid-state physicists and experts in extrinsic phenomena, and in 1961 and 1962 presented in a dozen papers a long series of new formulas, some of which are already being applied to specific problems.

The Soviet Union has the advantage in this endeavor not only of a centralized organization, but also of a larger number of solid state physicists than any other country. According to Conyers Herring's previously quoted estimates, based on 1960 figures, 24 percent of the world's solid state physicists are in the USSR as against 21 percent in the US. Because of this steadily growing number of highly skilled men, the Russians can also narrow their fields of specialization to, in some cases, relatively minor phenomena or single compounds.

A third point to consider is the decreasing use of recent foreign data by Soviet photovoltaic cell researchers. While they still seem to receive translations of all the more important recent papers published abroad, they now tend to cite more and more often only those foreign works that were produced before 1960, when the expansion of Soviet solid state physics began manifesting itself.

A rough survey shows that, while the proportion of non-Soviet to Soviet works published between 1955 and 1959 cited by Russian authors in 1962 was about 6:1, the same authors quoted in the same papers more Soviet than non-Soviet works published in 1960 and after.

A curious method of handling science information was shown in the present report in the review of a series of papers on cadmium telluride research. This was published over a period of four years by a team of researchers, Vodakov, Lomakina, Naumov and Maslakovets. The latter was the man who nearly twenty years earlier built the most efficient photovoltaic cell of that time and has been since considered to be one of Russia's foremost experts in the field.

At first, in July 1957, a rather insignificant communication could be found in the Zhurnal tekhnicheskoy fiziki stating that the four researchers had obtained the modest efficiency of 2 percent from experimental cadmium telluride photoelements they had produced. After that the name of Maslakovets (who obviously must have headed the team) and of his three associates vanished from the pages of Soviet science journals for fully two and a half years until, in the January 1960 issue of the Fizika tverdogo tela they reappeared as authors of three extensive papers reporting on the most through investigations evermade of cadmium telluride solar cell material and claiming an efficiency of 4 percent. And again the name of Maslakovets, Lomakina and Vodakov vanished and could not be traced in any Soviet journal through the end of December 1962, the last month included in the present survey. However, the fourth member of the team, Naumov, emerged in December 1961 as coauthor (with an unknown woman scientist Nikolayeva) of the shortest communication ever published by Fizika tvordogo tela, stated that an efficiency of 6 percent had been obtained from an experimental cadmium telluride photovoltaic solar cell.

If the approach evidenced by this particular case for the release of scientific data can be considered as part of a pattern, then interesting indications may be inferred from certain names lost to view from the pages of Soviet science journals after they showed up heading some particular research. The underscored names of Soviet scientists in the appendix to the present report should provide help in such inquiries because they are those of the top men who usually direct groups of science workers performing important tasks.

With the exception of one short paper by Kolomiyets, no direct mention of variable-gap photoelements was found in the literature of the reviewed period. This omission is the more puzzling, because, according to Soviet writers it was Ioffe who many years ago first proposed a photo-voltaic cell in the form of superimposed germanium-silicon-cadmium telluride layers. In view of the detailed descriptions of other methods used by the Russians to bring up the efficiency and reduce the price of the photovoltaic cell materials, the most plausible explanation appears to be that in the Soviet Union this research is classified.

As to the basic question of the quality of Soviet photovoltaic cells for solar energy conversion, one could conclude at the beginning of 1963 that the best the Russians had were still silicon instruments, highly resistant to radiation and having an efficiency of about 15 percent. It seems probable that they experimented with some form of light concentrators on their Cosmos series spacecraft. The reported fact that early in 1961 they obtained a 6 percent efficiency of cadmium telluride photoelements and that since then nothing has been heard of the Maslakovets team may be an indication that experiments were made in space with cadmium telluride instruments.

To sum up, the Russians, who see a major economic advantage in a rapid development of photovoltaic cells particularly for large-scale power production, seem to make great strides in comprehending and mastering the photovoltaic effect in semiconductors. Though at the present stage any breakthroughs seem to be unlikely, it would not be surprising if, considering the quality and number of researcers employed, Soviet scientists were at the point of demonstrating significant advances.

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^{*} FTT = Fizika tverdogo tela. QC176.A1F5

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APPENDIX: RESEARCH INSTITUTES AND PERSONNEL

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Name	Specialization	References
Agayev, Ya.	Electrical properties of solids.	120, 121
Arkad'yeva, Ye. N.	Extrinsic properties of semiconductors.	24, 25, 27
Berkovskiy, F. M.	Extrinsic properties of semiconductors.	28, 45
Burdudov, Yu. M.	Gallium arsenide.	93
Galavanov, V. V.	Indium antimonide.	104, 117, 119
Gubanov, A. I.	Electron states; semi- conductors; amorphous semiconductors.	11, 12
Imenkov, A. N.	Gallium arsenide.	93
Ivanov, Yu. L.	Extrinsic properties of semiconductors.	
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Khansevarov, R. Yu.	Extrinsic properties of semiconductors.	20, 21
Khartsiyev, V. Ye.	Electron states; electrical properties in solids; complex semiconductors.	8, 97
Kiseleva, N. R.	Indium antimonide; gallium antimonide.	123

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Mashovets, T. V.	Silicon; germanium.	31, 32
Melannikova, Yu. S.	Indium antimonide.	110
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Paritskiy, L. G.	Extrinsic properties of semiconductors; electrical properties of solids.	20, 22, 23, 27, 142
Pronina, M. P.	Gallium arsenide; indium antimonide; indium phosphide; magnetic properties of solids.	105
Rogachev, A. A.	Electrical properties of solids; cadmium selenide; gallium arsenide.	96, 97, 142

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Tsarenkov, B. V.	Gallium arsenide.	93, 95, 96, 97
Vinogradova, K. I.	Indium antimonide.	104, 119
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Yaroshetskiy, I. D.	Extrinsic properties of semiconductors.	20, 21
Yemel'yanenko, O. V.	Gallium arsenide; indium antimonide.	29, 98, 99, 113, 116
Zakharchenya, B. P.	Cadmium sulfide.	149
Zolotarev, V. F.	Indium antimonide; magnetic properties of solids.	111, 112, 114, 115, 118

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Boltaks, B. I.	Silicon; cadmium telluride (1955).	58
Dubrovskiy, G. B.	Optical properties of solids; cadmium telluride; silicon photoelements (1956)	56, 79, 80, 81
Fedorus, G. A.	Cadmium sulfide; cadmium selenide.	133, 159, 166
Fursenko, V. D.	Cadmim sulfide	159 , 165
Gliberman, A. Ya.	Silicon photoelements	57 , 67, 68

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Landsman, A. P.	Silicon photoelements; solar power stations; solar batteries for Sputnik III (?	7, 55, 63, 67, 68).
Lomakina, G. A.	Cadmium telluride photo- elements.	74, 75, 76, 77
Marchenko, A. I.	Cadmium sulfide.	159
Maslakovets, Yu. P.	Cadmium telluride photo- elements; silicon photo- elements; solar cell batteries for early sputniks (?); tallium sulfide photo- elements (1938).	74, 75, 76, 7 7, 79
Matveyeva, N. N.	Silicon.	58.
Naumov, G. P.	Cadmium telluride photo- elements.	74, 75, 76, 77, 78
Nikolayeva, O. V.	Cadmium telluride photo- elements.	78
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Subashiyev. V. K.	Silicon; silicon photo- elements; p-n junctions; silicon solar batteries for Sputnik III (?).	7, 39, 40, 55, 56, 79,
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Vodakov, Yu. A.	Cadmium telluride photo- elements.	7 4 , 75, 76, 77
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